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Information is provided regarding the nature, magnitude, and extent of the emissions of zinc in the United States for the year 1969. Background information concerning the basic characteristics of the zinc industry has been assembled and included. Brief process descriptions are given; they are limited to the areas that are closely related to existing or potential atmospheric losses of the pollutant. The zinc emissions and emission factors are based on data obtained from production and reprocessing companies. Additional information was acquired during field trips to inspect the air pollution control equipment and observe processing operations. Emissions to the atmosphere during the year were 159,922 tons. About 31 percent of the emissions resulted from the metallurgical processing of zinc, more than 30 percent from the production of iron and steel, and nearly 18 percent from the incineration of refuse. The production of zinc oxide, the wear of rubber tires, and the combustion of coal were also significant emission sources.

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APTD-1139

REPORT

NATIONAL INVENTORY OF SOURCES AND EMISSIONS BARIUM, BORON, COPPER, SELENIUM, AND ZINC

1969

for

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR PROGRAMS
CONTRACT NO. 68-02-0100

ZINC

SECTION V

by

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May 1972

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PREFACE

This report was prepared by W. E. Davis & Associates pursuant to Contract No. 68-02-0100 with the Environmental Protection Agency, Office of Air Programs.

The inventory of atmospheric emissions has been prepared to provide reliable information regarding the nature, magnitude, and extent of the emissions of zinc in the United States for the year 1969.

Background information concerning the basic characteristics of the zinc industry has been assembled and included. Process descriptions are given, ~~but~~ they are brief, and are limited to the areas that are closely related to existing or potential atmospheric losses of the pollutant.

Due to the limitation of time and funds allotted for the study, the plan was to personally contact all of the primary producers and about twenty percent of the companies in each major emission source group to obtain the required information. It was known that published data concerning the atmospheric emissions of zinc were virtually nonexistent, and contacts with industry ascertained that atmospheric emissions were not a matter of record. The zinc emissions and

emission factors ~~that are presented~~ are based on the summation of data obtained from production and reprocessing companies. Additional information was acquired during field trips to inspect the air pollution control equipment and observe processing operations.

ACKNOWLEDGEMENTS

This was an industry oriented study and the authors express their appreciation to the many companies and individuals in the zinc industry for their contributions.

We wish to express our gratitude for the assistance of the various societies and associations, and to the many branches of the Federal and State Governments.

Our express thanks to Mr. C. V. Spangler, Project Officer, EPA, Office of Air Programs, Research Triangle Park, N. C., for his helpful guidance.

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SUMMARY

The flow of zinc in the United States has been traced and charted for the year 1969 (Figure I). The consumption was 1,797,000 tons, while primary and secondary production totaled 1,417,000 tons. Imports and exports were 354,000 and 43,000 tons, respectively. Ore used directly in processing was 127,000 tons.

Emissions to the atmosphere during the year were 159,922 tons (Table I). About 31 percent of the emissions resulted from the metallurgical processing of zinc, more than 30 percent from the production of iron and steel, and nearly 18 percent from the incineration of refuse. The production of zinc oxide, the wear of rubber tires, and the combustion of coal were also significant emission sources.

Emission estimates for mining, production of primary and secondary zinc, manufacture of zinc-base alloy products, and the production of zinc oxide are based on unpublished data obtained from industrial sources.

TABLE I

EMISSIONS BY SOURCE
1969

Source Category	Source Group	Emissions - Tons		Emissions %
Mining and Milling			72	--
Metallurgical Processing			50,000	31.3
Secondary Production			3,800	2.4
End Product Uses			23,270	14.6
	Zinc-Base Alloys	3,000		
	Zinc Coatings	950		
	Brass and Bronze	180		
	Zinc Oxide			
	Zinc Oxide Production	8,100		
	Rubber Tires	8,400		
	Photocopying	1,500		
	Paint	10		
	Other	1,000		
	Zinc Sulfate	30		
	Miscellaneous	100		
Other Emission Sources			82,780	51.7
	Coal	4,310		
	Oil	450		
	Iron and Steel			
	Blast Furnace	1,070		
	Open-Hearth Furnace	39,000		
	Basic Oxygen Furnace	900		
	Electric Furnace	7,400		
	Foundries	1,700		
	Incineration	27,950		
TOTAL			159,922	100.0

TABLE II

EMISSIONS BY REGIONS

	Tons
Region No. 1	19,800
Region No. 2	47,200
Region No. 3	52,500
Region No. 4	40,422
TOTAL	159,922

Region No. 1

Arizona
California
Colorado
Idaho
Montana
Nevada
New Mexico
Oregon
Utah
Washington
Wyoming

Region No. 2

Illinois
Indiana
Iowa
Kansas
Michigan
Minnesota
Missouri
Nebraska
North Dakota
Ohio
South Dakota
Wisconsin

Region No. 3

Alabama
Arkansas
Delaware
Florida
Georgia
Kentucky
Louisiana
Maryland
Mississippi
North Carolina
Oklahoma
South Carolina
Tennessee
Texas
Virginia
West Virginia
District of Columbia

Region No. 4

Connecticut
Maine
Massachusetts
New Hampshire
New Jersey
New York
Pennsylvania
Rhode Island
Vermont

EMISSION FACTORS

The emission factors presented herein are the best currently available. They were determined through a combination of methods consisting of: (1) direct observation of emission data and other related plant processing and engineering data; (2) estimates based on information obtained from literature, plant operators, and others knowledgeable in the field; (3) calculations based on experience and personal knowledge of metallurgical processing operations; and, (4) specific analytical results where available.

The basic data used to calculate the emission factors are contained in the files of the Contractor.

TABLE III

EMISSION FACTORS

Mining and Milling	0.2 lb/ton zinc mined
Metallurgical Processing	
Electrolytic Plants	60.0 lb/ton of product
Vertical-Retort Plants	80.0 lb/ton of product
Horizontal-Retort Plants	170.0 lb/ton of product
Secondary Production	20.0 lb/ton of zinc produced
End Product Uses of Zinc	
Zinc-Base Alloys	10.0 lb/ton of zinc processed
Zinc Coatings	4.0 lb/ton of zinc processed
Brass and Bronze	2.0 lb/ton of zinc content
Zinc Oxide Production	60.0 lb/ton of zinc oxide
Rubber Tire Wear	4.2 lb/million miles
Other Emission Sources	
Coal	17.0 lb/1,000 tons of coal burned
Oil	1.4 lb/1,000 bbls of oil burned
Blast Furnaces	0.02 lb/ton of pig iron produced
Open-Hearth Furnaces	1.3 lb/ton of steel produced
Basic Oxygen Furnaces	0.03 lb/ton of steel produced
Electric Furnaces	0.74 lb/ton of steel produced
Foundries	0.18 lb/ton of process weight

SOURCES OF ZINC

Zinc is a relatively soft bluish-white metal that is widely distributed in the earth's crust in the form of its various minerals. It is usually found in nature as the sulfide and occurs in small quantities in nearly all igneous rocks. The principal mineral is sphalerite, commonly called zinc blende, which is resinous in appearance with its color varying from light tan to black.

Most other zinc minerals have probably been formed as oxidation products of the sulfide. These minerals include zincite, goslarite, smithsonite, hemimorphite, willemite, franklinite, and hydrozincite. They are usually minor sources of zinc; however, franklinite and zincite are major deposits in the ores of Sussex County, New Jersey.

Zinc minerals are commonly associated with lead minerals and the ratio of zinc to lead varies over a wide range. In the southeastern part of Missouri the ratio is in the order of 10 percent zinc and 90 percent lead, but in the southwestern part of Missouri the ratio is about 82 percent zinc to 18 percent lead. Other minerals that are associated with zinc are calcite, dolomite, pyrite, greenockite, quartz, chalcopyrite, and barite.

In the United States ores containing zinc are mined in Arizona, California, Colorado, Idaho, Illinois, Kansas, Missouri, Montana, New Jersey, New Mexico, New York, Oklahoma, Pennsylvania, Tennessee, Utah, Virginia, Washington, Wisconsin, and to a lesser extent in several other states. About 44 percent of the zinc from domestic mines during 1969 was from states west of the Mississippi River. Approximately 63 percent was contained in zinc ores; 18 percent in lead-zinc ores; 9 percent in lead ores; 6 percent in copper-lead-zinc ores; and 4 percent in all other ores.

During 1969 zinc produced from domestic ores accounted for about 31 percent of the United States' consumption; zinc from foreign ores about 34 percent; imported slab zinc about 18 percent; and secondary zinc about 17 percent. The foreign ores and concentrates were principally from Canada, Mexico, and Peru. The major part of the imported slab zinc was from Canada, Japan, Australia, Peru, Belgium-Luxembourg, and Mexico.

MATERIAL FLOW THROUGH THE ECONOMY

The consumption of zinc in the United States during 1969 was 1,797,000 tons [1], which was nearly 4 percent higher than in 1968. The sources of supply were principally primary slab zinc (1,041,000 tons - Zn content) recovered from foreign and domestic ores, secondary zinc (376,000 tons - Zn content) reclaimed from old and new scrap, and imports of metal and compounds (354,000 tons - Zn content) [1] as shown in Figure I.

The largest use of zinc was in zinc-base alloys. About 33 percent was utilized for this purpose, principally in diecasting alloy. The second largest quantity, nearly 27 percent, was consumed by the galvanizing industry. The amount entering into brass and bronze production was 21 percent, while that in zinc oxide was only 10 percent.

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1. Minerals Yearbook: Bureau of Mines; 1969.

ZINC

MATERIAL FLOW THROUGH THE ECONOMY - 1969

(Thousand Tons - Zn Content)

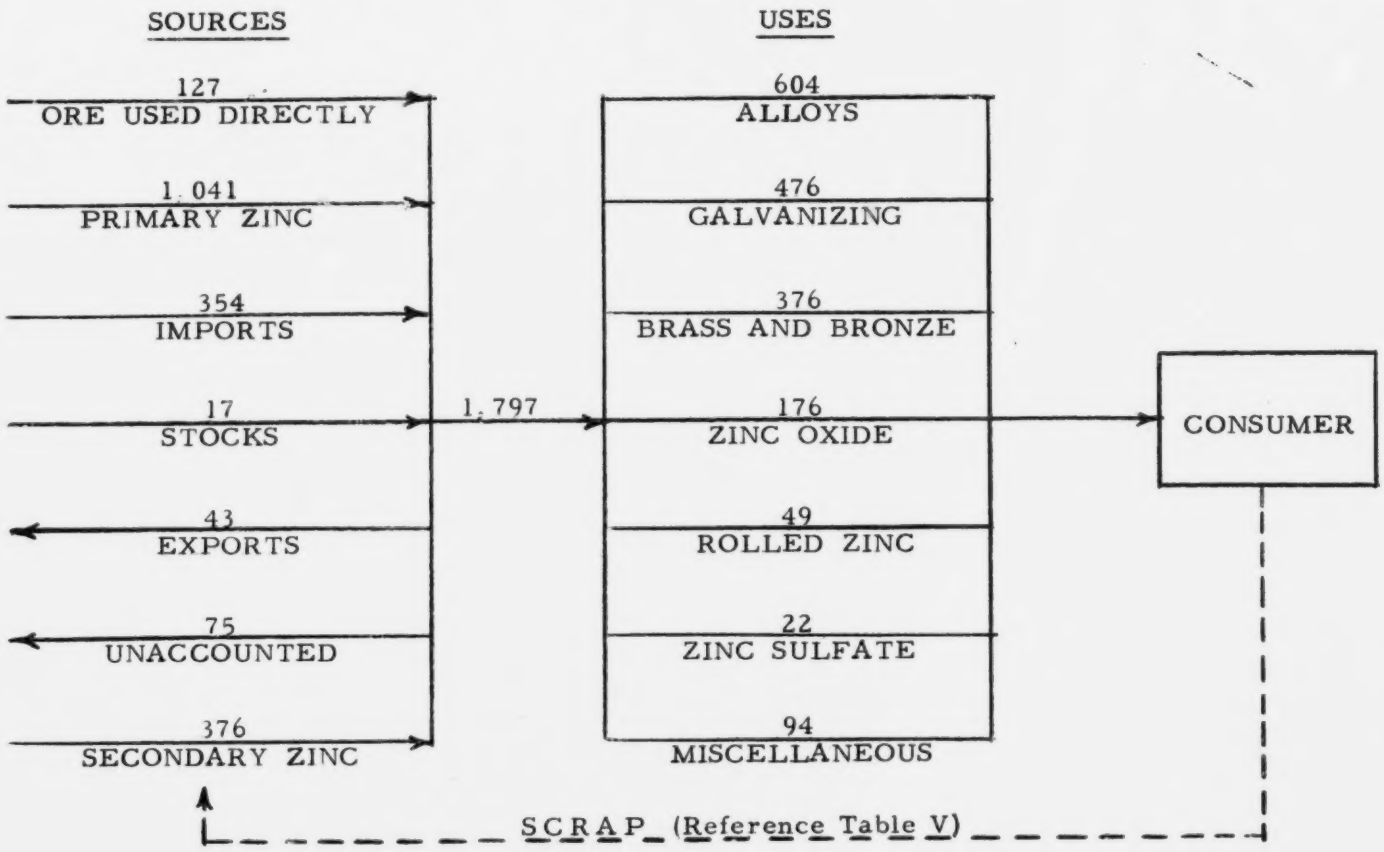

Figure I

USES AND EMISSIONS OF ZINC

MINING AND MILLING

Even though mining methods vary somewhat with the type of ore body, the basic operations of ore removal, ore handling, and crushing are essentially the same. Following crushing, the usual practice is for all of the ore to be ground in ball mills and separated by flotation; however, certain western ores require a different treatment. They contain lead and zinc too intimately mixed for satisfactory separation by flotation and the final step in this case involves sulfuric acid leaching usually at an electrolytic zinc plant.

From the standpoint of emissions to the atmosphere, the principal losses during mining and milling operations are those that occur due to blasting, ore handling, crushing, and the wind loss from tailings. During grinding and flotation or leaching, the ore is wet and atmospheric emissions are negligible.

While this study was in progress, many companies were contacted concerning their mining methods and the zinc emissions that occur during mining and milling. Even though

records were not available concerning losses to the atmosphere, several emission sources were observed at each location that was visited.

Emissions from Mining and Milling - Zinc emissions to the atmosphere from sources of mining and milling are estimated by the Contractor at 0.2 pound per ton of zinc mined. The actual zinc content of the ore mined in the United States during 1969 was about 723,000 tons, and zinc emissions to the atmosphere were 72 tons.

METALLURGICAL PROCESSING

In the United States, during 1969, zinc was produced at 14 primary slab zinc plants. Those plants produced primary zinc, secondary zinc, and various zinc compounds including large quantities of zinc oxide. Zinc was also reclaimed from old and new scrap at 13 secondary slab zinc plants, and from lead smelter slag at 5 slag-fuming plants.

The primary zinc smelters are all somewhat different, but are usually classified according to 3 general types. Five of them are electrolytic plants, 5 others are horizontal-retort type distillation facilities, and the remaining 4 are vertical-retort distillation units.

Regardless of the type of recovery process employed at the different plants, many of the operations are similar. Roasting in some form is practiced on all zinc sulfide concentrates and drying prior to roasting is often required. The exothermic heat of reaction of the sulfur in the ore with the oxygen of the air is the source of heat for processing; however, natural gas is used as auxiliary fuel, principally for plant start-up purposes. Typically, zinc recovery procedures include ore and concentrate unloading from railroad cars to open storage

piles, loading and conveying from storage to dryers, conveying from dryers to storage bins, and on to roasters. Several types of dryers and roasters are used at the various locations.

Of the several types of roasters listed in Table IV, the Ropp roaster is the oldest currently used in the zinc industry. It is a long, narrow, mechanically rabbled reverberatory furnace divided into 2 parallel hearths. The multiple hearth is the next oldest type and it is about 20 or 25 feet in diameter containing from 7 to 16 hearths. Both roasters operate at relatively low temperatures, discharging large volumes of offgas.

Suspension and fluid-bed roasters are more recent developments and they operate at higher temperatures. The suspension roaster consists of a refractory-lined vessel with a large combustion space in the top and 4 hearths in the bottom portion. The process resembles the burning of pulverized coal. Even though the offgas volume is relatively low, there is a large amount of dust discharged from the suspension roaster. Fluid-bed roasters also have these same operating characteristics.

After roasting at electrolytic plants, the concentrate is

TABLE IV

TYPICAL ZINC ROASTING OPERATIONS (1)

Type of Roaster	Operating Temp. F	Feed Capacity ton/day	Dust in Offgas % of Feed	Offgas SO_2 %
Multihearth	1,200-1,350	50-120	5-15	4.5-6.5
Multihearth (2)	1,600-1,650	250	5-15	4.5-6.5
Ropp (3)	1,200	40-50	5	0.7-1.0
Fluid bed (4) (Dorr-Oliver)	1,640	140-225	70-80	7-8
Fluid bed (2) (Dorr-Oliver)	1,650	240-350	75-85	10-12
Fluid bed (Lurgi)	1,700	240	50	9-10
Suspension	1,800	120-350	50	8-12
Fluid column	1,900	225	17-18	11-12

(1) Dead roast except where noted otherwise.
(2) First stage is a partial roast in multihearth; second stage is a dry-feed dead roast in Dorr-Oliver fluid bed.
(3) Partial roast.
(4) Slurry feed.

"Systems Study for Control of Emissions Primary Nonferrous Smelting Industry"; Vol. I: Arthur G. McKee & Co., San Francisco, Calif.; June, 1969.

leached with dilute sulfuric acid as shown in Figure II to form a zinc sulfate solution. Then the pregnant liquor is purified and piped to electrolytic cells, where the zinc in the liquor is deposited on aluminum cathodes. At intervals the cathodes are removed from the cells and stripped of zinc. After the pregnant liquor is purified, the residue that remains is washed, dewatered, and dried as it is prepared for the recovery of other metals.

After roasting at distillation plants, sintering is used mainly to agglomerate the roaster calcine. The sintering machines have continuous conveyors upon which the feed material is placed and processed. The feed is normally a mixture of calcine or concentrates, recycled ground sinter, and the required amount of carbonaceous fuel, each of which is pelletized and sized before it is fed to the machines and ignited. During processing the combustion gas and large quantities of dust are carried away from the sintering machines. Usually 5 to 10 percent of the total feed appears as dust in the gas that is discharged.

At horizontal-retort distillation plants, processing is a batch-type operation. The horizontal retorts are small ceramic

ELECTROLYTIC ZINC PLANT FLOW DIAGRAM

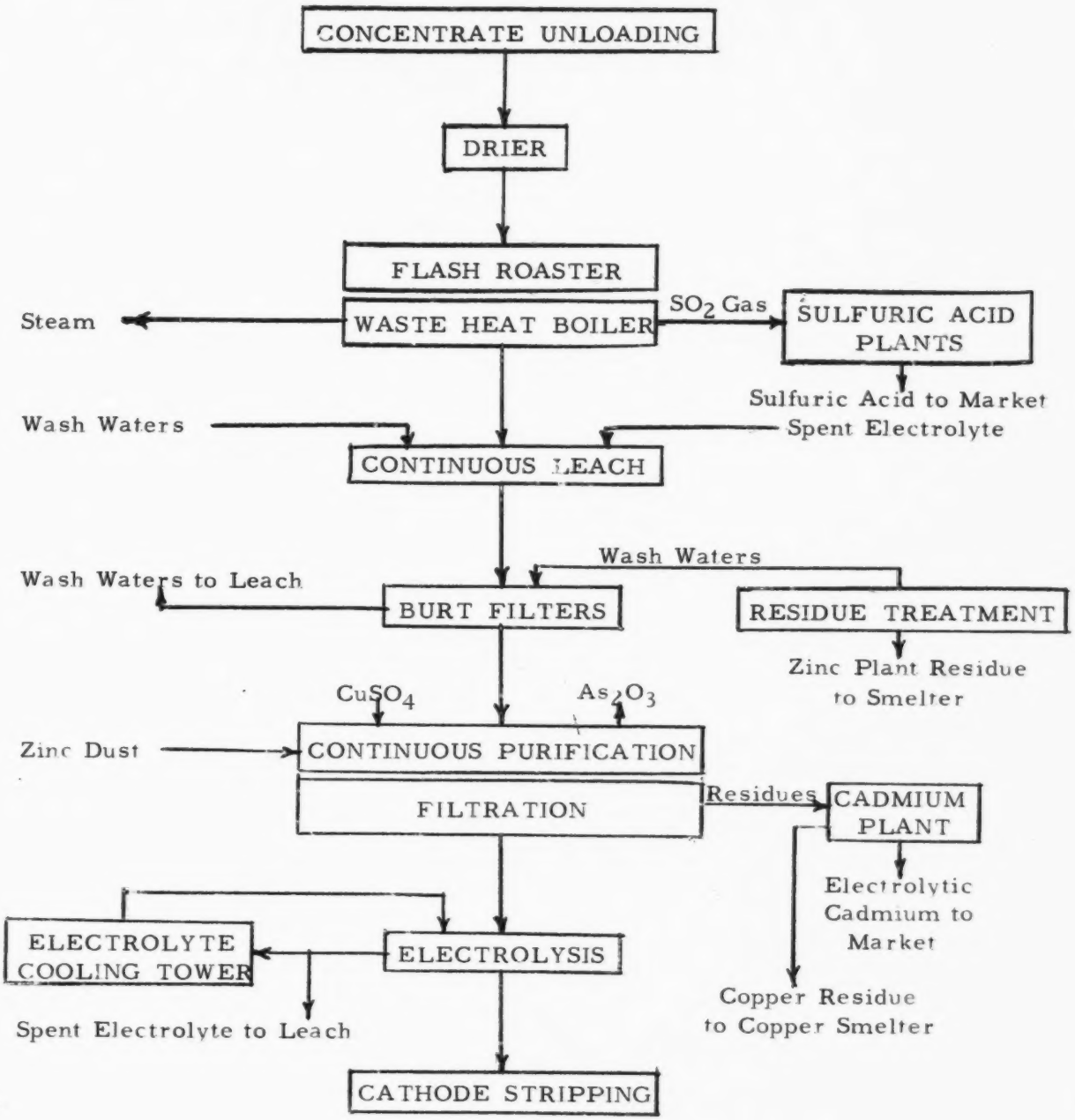

Figure II

cylinders that are mounted horizontally in furnaces that hold several rows of retorts mounted one above the other. They are heated by passing hot combustion gases through the spaces around the outside. The charge of zinc-bearing material and reduction fuel is contained inside and is subjected to prolonged exposure to the reducing atmosphere at a temperature of about 2,000 F.

When smelting is ready to begin, the retorts are charged and condensers are placed over the ends to condense the majority of the zinc vapor emerging. The mouths of the condensers are stuffed with charge or other available high-zinc material, almost completely sealing the outlet. Heavy firing is started and gas is allowed to escape through one small hole in the stuffing. About 6 hours after starting, the first zinc begins to come off the charge and the condensers must perform their functions. The formation of blue powder takes place if the temperature is low enough to prevent the escape of uncondensed zinc. If it is high enough to minimize blue powder formation, then there is appreciable loss of vapor. In foreign plants this fact has led to the use of condensing devices called prolongs, which are designed to recover the escaping vapor as blue powder. Prolongs increase

zinc recovery about 2 or 3 percent, but in the United States the cost of using them is usually considered to be greater than the value of the extra recovery.

The vertical-retort process is a continuous method for producing high-purity zinc by pyrometallurgical means. High boiling-point impurities such as lead and low boiling-point impurities such as cadmium can be separated from relatively impure zinc.

The vertical-retort furnaces consist of 3 major sections: the charge column, the reflux section, and the combustion-heating chamber. The charge, which consists of hot briquettes, enters the charge column through a door located near the top. During charging, effluent from the retort is exhausted directly to the atmosphere through a short stack located on top of each retort. The charge moves down through the combustion or heating zone of the column and heat produced in the combustion chamber is transferred through the refractory walls of the column to the charge. Gases leaving the retort section of the heating zone contain zinc vapor, carbon monoxide, and particulates driven from the briquettes. The gases pass out the top of the column to a condenser where

the zinc is condensed from the gas stream. Next, the gas is scrubbed and recycled to the combustion zone.

At all zinc smelters visited during this study, bag filters and/or electrostatic precipitators were employed as the principal dust collection devices; however, cyclone collectors and scrubbers were also used at some locations. At all plants there were some emission sources that were uncontrolled. There was virtually no control in connection with concentrate unloading, handling, and storage.

Very few operators were found who actually knew the particle size of the zinc emissions. The few reports obtained showed the particle size as ranging from less than 0.5 to 100 microns. At one horizontal-retort plant, the retort fumes were reported to be as follows: 34 percent less than 2.5 microns; 35 percent between 2.5 and 5.0 microns; and 31 percent larger than 5 microns. The emissions are composed of zinc oxide and sulfur complexes.

Emissions from Metallurgical Processing During 1969 zinc emissions to the atmosphere resulting from metallurgical processing of zinc-bearing ores and concentrates totaled 50,000 tons. This estimate is based on emission and material

balance data obtained from processing companies during field trips to primary slab zinc plants.

Zinc emission factors based on the data obtained are as follows:

Type of Plant	Pounds Zn Emissions per Ton Zn Produced
Electrolytic zinc plant	60
Vertical-retort zinc plant	80
Horizontal-retort zinc plant	170

SECONDARY ZINC PRODUCTION

In the United States the production of secondary zinc is important. During the recent years it has accounted for more than 20 percent of the total supply. It is produced in both alloyed and unalloyed forms from old and new scrap, as shown in Table V.

Zinc scrap is processed in several different ways. Some is redistilled at primary and secondary zinc plants. Some is vaporized in furnaces and then converted to zinc oxide in suitable combustion chambers. Some is processed in retorts and condensed to slab zinc or zinc dust. However, about 50 percent of the zinc in scrap is in the brass that is remelted by brass and bronze producers for the production of more brass.

When dealing with scrap metal, various problems are involved that are different than those encountered when dealing with ores and concentrates. There are many types of scrap and some are relatively pure whereas others are alloys containing varying amounts of zinc. Even though scrap metal may be pure zinc, it is often intimately associated with non-metallic materials such as chemicals, dirt, grease,

TABLE V

ZINC RECOVERED FROM SCRAP PROCESSED IN THE UNITED STATES DURING 1969 [1]/

(Short Tons)

Kind of Scrap	
New Scrap:	
Zinc-base	134,668
Copper-base	156,381
Other	3,715
TOTAL	294,764
Old Scrap:	
Zinc-base	40,284
Copper-base	37,975
Other	3,368
TOTAL	81,627

Form of Recovery	
As metal	107,557
In zinc-base alloys	19,980
In brass and bronze	196,244
In other alloys	7,312
In chemical products	45,298
TOTAL	376,391

1- Minerals Yearbook Bureau of Mines; 1969.

insulation, moisture, oil, paint, plastics, rubber, and many others.

Raw material preparation is an important operation in scrap metal processing. The dealers must first identify and sort the scrap, then it must be further inspected and sorted when it is received at smelters, brass mills, and other processing facilities. After sorting, some of the material is pretreated mechanically and some requires a preliminary furnace treatment. Such treating prior to smelting is usually at a rather low temperature and various types of furnaces may be employed. A muffle furnace or kiln may be used to drive off moisture, oil, and other organic impurities. After the raw material has been prepared the remaining procedures for melting and refining are principally material handling and pyrometallurgical operations utilizing cupolas, crucibles, reverberatories, and other types of furnaces. There is no basic difference in the melting and refining actions in these furnaces, but there are differences in the alloys processed, the furnace capacities, the condition of charge materials, and the methods for heating.

From the standpoint of zinc emissions to the atmosphere, the

remelting of bronze does not hold great interest. Copper and tin are the principal elements in a true bronze and the quantity of zinc is low, usually less than 5 percent. Also, the boiling points of copper and tin are above 4,000 F while the normal pouring temperature is in the range of 2,000 to 2,200 F. The remelting of brasses containing 15 to 40 percent zinc, however, presents a different situation. The pouring operations are carried out at temperatures that are near the boiling points (about 2,200 F) and there is some vaporization.

Zinc is melted in crucible, pot, kettle, reverberatory, or electric-induction furnaces and is reclaimed from higher melting point metals in sweat furnaces. Secondary refining of zinc is carried out in retort furnaces. This reduction process is used to reclaim zinc from the dross formed in zinc-melting operations, the zinc oxide collected by air pollution control systems, and the contaminated zinc oxide from zinc oxide plants.

The emissions of zinc and other pollutants vary in composition and concentration during the operating cycle of the retorts. At first there are few, if any, zinc emissions. The

charge is moist and steam is emitted as the retorts are heated. After several hours when zinc begins to form, both carbon monoxide and zinc vapors are discharged. During the heating cycle, zinc is poured from the condensers about 3 times and each time the emission of zinc vapors increases. At the end of the cycle, zinc fumes and dust are discharged to the atmosphere as the spent charge is removed. As the zinc vapors mix with air, they oxidize and form a dense white cloud of zinc oxide fumes.

Emissions from Secondary Zinc Production - There are large variations in the concentrations of zinc fumes that are discharged to the atmosphere during the production of secondary zinc. Emissions from brass melting operations may vary from less than 0.5 percent to 6 percent of more of the total metal charge [1], and 2 to 15 percent of the zinc content [2]. Uncontrolled particulate emissions have been reported to range from 1 to 70 pounds per ton of

---

1- St. John, H. M., "Melting Practice in the Brass Foundry"; Foundry, 83; Nov., 1955.

2- Allen, G. L.; Viets, F. H.; McCabe, L. C., "Control of Metallurgical and Mineral Dusts and Fumes in Los Angeles County, California" Bureau of Mines; Info. Circ. 7627 Apr., 1952.

charge [1] [2], whereas controlled emissions range from 0.1 to 1 pound per ton of charge [2].

Chemical analyses of dust collected in a brass and bronze smelter baghouse show the zinc content varies from 45 to 77 percent [3]. Another report on a series of tests in Los Angeles County indicated the zinc oxide content of tume from representative red and yellow brass furnaces averaged 59 percent [4].

Data obtained from industry during this study indicates that zinc emissions to the atmosphere during the production of secondary zinc vary from 0.01 to 124 pounds per ton of product, averaging 20 pounds per ton. During 1969 zinc emissions to the atmosphere totaled 3,800 tons.

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1 "Air Pollutant Emission Factors"; Environmental Protection Agency; Preliminary Document; Apr., 1971.

2 Air Pollution Engineering Manual; Public Health Service Publication No. 999-AP-40, 1967.

3 Spendlove, Max J.; "Methods for Producing Secondary Copper"; Bureau of Mines; Info. Circ. 8002; 1961.

4 Allen, G. L.; Viets, F. H.; McCabe, L. C.; "Control of Metallurgical and Mineral Dusts and Fumes in Los Angeles County, California"; Bureau of Mines; Info. Circ. 7627; Apr., 1952.

END PRODUCT USES OF ZINC

In the United States during 1969 about 29 percent of the primary and secondary zinc was used in the commercially pure form, principally for galvanizing sheet, strip, tubes, pipes, fencing, structural shapes, and other steel articles. Approximately 55 percent was consumed as an alloying element in the production of zinc-base and copper-base alloys.

The largest application of zinc was in zinc-base die-casting alloys used extensively by the automotive industry. During 1969 the zinc consumed in the manufacture of automobiles was approximately 35 percent of the zinc produced.

Zinc-Base Alloys

Zinc-base die castings are now used extensively in several industries since the great advancements made by the die-casting industry itself during the last 30 years. Products with good stability, easy machinability, attractive appearance, and reasonable cost are now easily formed. The automobile industry uses 55 to 60 percent of the die-casting production in such items as carburetors, fuel pumps, door handles, radiator grills, windshield-wiper motors, and other interior and exterior hardware. The home appliance producers also make good use of zinc-base die castings in sewing machines, ironers, washing machines, radio and television sets, and kitchen and food-mixing equipment. Additionally, commercial machines and tools, builders' hardware, office equipment and business machines, and optical and photographic equipment use a large variety of these castings.

There are only a few zinc-base alloys in use for die casting. Aluminum is the major alloying constituent used in quantities varying from 3.5 to 4.3 percent. A zinc-aluminum alloy imparts increased strength and slows the attack of the alloy on iron and steel parts. The amount of copper that may be used in a zinc base alloy varies some, but the usual quantity is

0.25 to 0.75 percent for increasing tensile strength and hardness. Magnesium reduces subsurface corrosion and counteracts harmful effects of small impurities. It is usually not added in amounts greater than 0.05 percent.

Virgin metals are always preferred when manufacturing the alloys for die casting. The procedure itself is usually accomplished in a pot or reverberatory furnace. The alloy is then cast into bars or pigs that fit the melting pots at the die-casting machine.

The actual die-casting machinery is generally well automated and is often a "hot chamber" machine because it is simpler and faster to operate. The zinc-base alloys are first melted in pots ranging in size from 2,000 to 8,000 pounds. The temperature of this metal in the pot should not exceed 800 F, and a good range is 300 to 400 F. The molten metal flows from the pots, filling an adjacent cylinder. A plunger is forced down pushing the metal from the cylinder into the die for the cast. The dies themselves are ordinarily made of high quality steel and filled at temperatures up to 950 F. The operation of this machine usually requires an operator to open and close the dies and remove castings.

At most plants the scrap generated during die-casting operations is remelted, cleaned, and reused. From the standpoint of air pollution, these reclaiming operations usually account for most of the emissions to the atmosphere. Normally induced draft ventilation systems are used, but there is no dust or fume collection equipment.

Slush castings are utilized only in a very small way as compared with die castings. Their primary purpose is in the production of hollow castings and they are mainly employed in the lighting fixture and novelty field. To make these castings, a metal shell is frozen on the inner surface of a split mold. The mold is inverted quickly so the molten metal flows away and the thin shell casting remains. The alloys used in these castings must have a fairly low freezing temperature and solidification over a range of temperatures. These alloys usually consist of 94 or 95 percent zinc, and the remainder is aluminum or aluminum and copper.

During this study the information obtained from die-casting companies indicates that zinc emissions to the atmosphere averaged about 10 pounds per ton of zinc processed, even though the range reported was from less than 10 to as much

as 60 pounds per ton. Based on the average of 10 pounds per ton, the atmospheric emissions in the United States in 1969 totaled 3,000 tons.

Zinc Coatings

Galvanizing - The hot-dip process is the most important galvanizing method used for coating clean iron and steel surfaces with a thin layer of zinc. It is adaptable to the coating of nearly all types of articles and the basic steps in the process are:

1 - Preparation of the metal surface by degreasing, rinsing, pickling, and rerinsing.

2 - Prefluxing by immersion of the metal in a tank of preflux.

3 - Galvanizing by immersion in a tank of molten zinc.

4 - Finishing by shaking or centrifuging, water quenching, deburring, and inspecting.

The galvanizing industry used 450,000 tons of slab zinc during 1969, which was 33 percent of the total slab consumption.

About half of the galvanized sheet produced is used by the building industry, but another important application is the production of automobile underbody parts. Familiar applications for galvanized steel are roofing sheet, guttering, culverts, fencing, pipe, wire, pole-line hardware, nails, pipe fittings, switch boxes, electrical conduit, tanks, and hot

water heaters. A growing use is for galvanized structural steel members for such structures as bridges and transmission towers.

The basic chemical factor in galvanization is that zinc readily combines with iron to form an alloy layer consisting of several layers, each increasing in zinc content from the steel to the surface. The galvanizing kettle is made of steel and either riveted or welded. The shape and size of the kettle are generally dependent on the work to be galvanized in them. Most kettles are side-fired and have a layer of lead on the bottom to reduce the reaction between the zinc bath and the iron of the kettle, and to improve heat distribution. When continuous operation is used, the average pot capacity is about 20 tons of zinc per ton of material galvanized per hour.

Prior to the actual zinc-coating bath, the steel to be coated may be immersed in a hrdrofluoric acid solution to dissolve grains of sand, and then a cleaning or pickling solution of sulfuric or hydrochloric acid. Superficial oxide may also be removed by passing the steel through a solution of 5 to 20 percent zinc ammonium chloride. Continuous sheet is given this zinc ammonium chloride bath, and then dried at about 350 to 550 F to a tacky state.

After these preliminary treatments, the steel passes into the zinc bath ranging from 840 to 860 F. As wire is coated, it must be held beneath the surface with sinker bars. Pipe is given a flux wash and then rolled into the galvanizing kettle. Small parts are generally handled in baskets and larger structural shapes are moved by crane. Continuous sheet passes into the molten zinc bath at about 840 F, and remains from 3 to 20 seconds for the desired coating.

Following the hot zinc bath, materials exit by different methods. Wire passes through asbestos pads or a charcoal bed, is cooled by water, and wound on a reel. Sheet leaves through exit rolls, cools, and then goes to leveling and finishing operations. Pipe is removed so that maximum drainage occurs from the inside, and then a blast of steam is used to remove excess zinc. Small parts are placed in a centrifuge in baskets to rid the excess zinc.

Final treatments may include blowing with a fume from burning sulfur or annealing immediately after the bath in a furnace as high as 1,200 F. For improved corrosion resistance and paint adhesion, chromate or phosphate treatments may be used. These subsequent treatments and variations in

operating conditions result in changes in the coating produced.

Zinc losses from drossing and skimming during galvanizing depend a great deal on the product. A loss occurs on pole-line hardware castings, which is usually greater than 25 percent of the zinc slabs melted. It may be as high as 50 percent if galvanizing bath time and temperature are not carefully observed. Sheet is generally the most economical with respect to losses, which usually amount to about 10 percent.

During hot-dip galvanizing operations most of the atmospheric pollutants are discharged when fresh flux is added, or when the flux cover is distrubed as it is each time an article is immersed into the zinc bath. Ammonium chloride is the principal pollutant; however, there are significant quantities of zinc, zinc oxide, and zinc chloride in the fumes, as shown in Table VI.

Processing operations at the galvanizing plants that were visited were similar, but the practices followed varied somewhat. In some instances the flux cover was agitated much more than in others, and no doubt emissions were substantially greater. There were no records of emissions and only 2 companies responded with emission estimates.

TABLE VI

CHEMICAL ANALYSIS OF THE FUMES COLLECTED BY A BAGHOUSE AND BY AN ELECTRIC PRECIPITATOR FROM ZINC-GALVANIZING KETTLES

Component	Fumes Collected in a Baghouse (Job Shop Kettle) wt. %	Fumes Collected in a Precipitator (Chain Link Galvanizing) wt. %
NH_4Cl	68.0	23.5
ZnO	15.8	6.5
$ZnCl_2$	3.6	15.2
Zn	4.9	--
NH_3	1.0	3.0
Oil	1.4	41.4
H_2O	2.5	1.2
C	2.8	--
Not Identified	--	9.2

"Air Pollution Engineering Manual", Public Health Service Publication No. 999-AP 40 p. 405 1967.

Based on observations and information obtained during this study, zinc emissions to the atmosphere due to galvanizing operations during 1969 are estimated at 4 pounds per ton of zinc processed, or a total of 950 tons.

Sherardizing - Another procedure for coating steel with zinc is called sherardizing. It has advantages over hot-dipped coatings for certain steel articles. There is only a slight dimensional change of an article during sherardizing permitting treatment of small parts such as nuts, bolts, washers, and small castings. Also, a sherardized coating is resistant to cracking, splitting, and flaking when the final article must be bent or worked.

In sherardizing, articles are placed in a metal drum and exceedingly fine particle-size zinc dust is added. The zinc dust is usually a small portion of new dust which has been added to used dust. The zinc content is between 80 and 92 percent, with the remainder being zinc oxide and other impurities. The drum is then sealed tightly to minimize zinc oxidation and prevent the escape of zinc vapor. Gas, oil, or electricity heats the drum as it slowly rotates, producing a uniform coating. The temperature ranges from 660 to 700 F and the coating thickness is determined by varying the treatment time from 3 to 12 hours. Sherardizing continues even during cooling, which is done slowly to prevent loss by exposing hot zinc dust to the atmosphere. Clean, metal surfaces are important therefore, a pickling operation followed

by cold and then hot water rinses is usually employed. If conditions are kept constant a uniform coating with a controlled thickness is produced.

Emissions to the atmosphere due to sherardizing are considered by the Contractor as negligible.

Electrolytic Deposition - Zinc can be deposited on sheet, wire, and all types of hardware electrolytically for corrosion protection. Zinc can be plated from a solution only because of its high hydrogen overvoltage and even then some substrates, such as cast iron, must be struck with tin or cadmium prior to zinc plating.

The zinc cyanide bath is used for general plating. However, zinc chloride, sulfate, and fluoborate baths are used in strip and wire plating because they are capable of higher plating speeds. A new pyrophosphate bath has also been introduced which eliminates the problem of cyanide disposal. Chromate post-treatment solutions are used for better appearance and performance.

Emissions to the atmosphere due to electrolytic deposition of zinc are considered by the Contractor as negligible.

Brass and Bronze

Brass is a copper alloy in which zinc is the principal alloying element, usually added in amounts up to 40 percent. The most used brasses of commerce are cartridge brass containing 30 percent zinc, and yellow brass containing about 35 percent. Bronze is also a copper alloy that contains zinc but normally the zinc content is not more than 5 percent.

About half of the zinc contained in the brass and bronze produced during 1969 was originally slab zinc, while the other half was recovered from scrap brass and bronze as described in the secondary zinc section of this report.

During the processing of brass and bronze the metals may be melted together in a crucible, rotary, or reverberatory furnace which may vary in size from several hundred to several thousand pounds in capacity. The metal is poured and cast at temperatures ranging from 1,200 to 2,400 F, the actual temperature depending upon the alloy. The molds used to form slabs, cakes, and billets are cast iron, water-cooled, and often copper-lined. After casting the shapes may be rolled into plate, sheet, and strip; extruded into rods, bars, and seamless tubes; or drawn into wire. Final

finishing operations include flattening, straightening, slitting, and cutting.

The emissions of zinc and other pollutants vary in composition and concentration with the type of furnace, the alloy, and the foundry practice as indicated by the data in Table VII.

During 1969 the slab zinc used in brass products totaled 179,469 tons [1], while the zinc emissions estimated by industry averaged 2 pounds per ton of zinc processed. Zinc emissions to the atmosphere for the year totaled 180 tons.

1- Minerals Yearbook; Bureau of Mines; 1969.

TABLE VII

BRASS-MELTING FURNACE
AND BAGHOUSE COLLECTOR DATA

Case	A	B	C
Furnace Data			
Type of furnace	Crucible	Crucible	Low-frequency induction
Fuel used	Gas	Gas	Electric
Metal melted	Yellow brass	Red brass	Red brass
Composition of metal melted, %			
Copper	70.6	85.9	82.9
Zinc	24.8	3.8	3.5
Tin	0.5	4.6	4.6
Lead	3.3	4.4	8.4
Other	0.8	1.3	0.6
Melting rate, lb/hr	388	343	1,600
Pouring temperature, F	2,160	2,350	2,300
Slag cover thickness, in.	1/2	1/2	3/4
Slag cover material	Glass	Glass	Charcoal
Baghouse Collector Data			
Volume of gases, cfm	9,500	9,700	1,140
Type of baghouse	Sectional tubular	Sectional tubular	Sectional tubular
Filter material	Orlon	Orlon	Orlon
Filter area, ft^2	3,836	3,836	400
Filter velocity, fpm	2.47	2.53	2.85
Inlet fume emission rate, lb/hr	2.55	1.08	2.2*
Outlet fume emission rate, lb/hr	0.16	0.04	0.086
Collection efficiency, %	93.7	96.2	96.0

*Includes pouring and charging operations

"Air Pollution Engineering Manual", Public Health Service Publication No. 999-AP-40, p. 274, 1967.

Zinc Oxide

Zinc Oxide Production - Zinc oxide is the principal zinc compound used by industry and 3 types are produced commercially in the United States, one being made by chemical processes and the other 2 utilizing pyrometallurgical procedures. The French process oxide, generally referred to as the indirect type, is characterized by its brightness, extreme whiteness, and a high degree of purity. The American process oxide, the direct type, is less bright and contains more impurities. The chemical processes produce secondary zinc oxides which are very pure, but are coarse and not as bright as either of the other 2 types.

When employing either of the pyrometallurgical procedures to produce zinc oxide, the ores and concentrates, or the scrap, must first be processed to produce zinc vapor. Then at that stage the vapor may be either condensed to produce slab zinc or oxidized to make American process zinc oxide. If the French process oxide is the desired product the vapor is condensed to form metallic zinc, after which the metal is vaporized and oxidized to form the product.

Zinc oxide is produced at primary and secondary smelters.

Information obtained from both types of plants indicates that zinc emissions to the atmosphere during the production of zinc oxide ranges from 20 to 170 pounds of zinc per ton of product. Based on a weighted average of 60 pounds per ton, the emissions during 1969 totaled 8,100 tons.

The manufacture and use of consumer products containing zinc oxide is also very important from the standpoint of zinc emissions to the atmosphere. During 1969 more than 220,000 tons were used in the manufacture of abrasives, adhesives, agricultural products, catalysts, ceramics, cosmetics, dental cements, feed additives, floor coverings, glue, insect repellents, lubricants, paints, pharmaceuticals, photocopying supplies, plastics, printing ink, pyrotechnics, rubber products, soaps, textiles, vitamins, and other items including various zinc compounds.

Rubber - The largest use of zinc oxide at the present time is in rubber products, principally as an activator in the vulcanization process. There are other properties, however, that also contribute to its popularity as a compounding ingredient. It helps to protect rubber by its opaqueness to ultraviolet light and by its high thermal conductivity.

During the manufacturing process the additives to be compounded into the rubber must be homogeneously dispersed throughout the blend. Rubber mills and Banbury mixers are the principal items of equipment employed for this purpose and it is at these locations where some zinc oxide emissions occur. The remaining steps include several forming and shaping procedures prior to the vulcanization process in which the plastic raw material is converted to an elastic state. The significant emissions of zinc that occur during the production and use of rubber products are those that are due to the wear of vehicle tires.

The usual dosage of zinc oxide is in the range of 60 to 100 pounds per ton of rubber and the average quantity per vehicle tire has been reported to be about 0.5 pound (Zn content - 0.4 pound). During 1969 motor travel in the United States

was about 1.05×10^{12} miles including passenger cars, motorcycles, buses, and trucks. On the average, the life of a tire is 20,000 miles and when replaced, 20 percent of the rubber is worn away [1]. Calculated on the basis of 4 tires per vehicle, the zinc emissions due to the wear of tires during 1969 totaled 8,400 tons.

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1. Private communication.

Photocopying - The second largest use of zinc oxide is in photocopying where its photoconductive and electrostatic properties are used to advantage. Conventional printing paper is coated with zinc oxide paint which is then made light sensitive by subjecting it to a negative corona discharge. The copy is made by placing the material to be reproduced between a light source and the charged paper. Where the light passes through to the zinc oxide paper, the electrostatic charge is dissipated. The image is readily developed by applying a pigmented resin powder that adheres only to the areas where the electrostatic charge has not been removed. The image is finally fixed to the paper by heating.

During 1966 through 1969 an average of 15,000 tons of zinc per year were used in photocopying, and the emissions resulting from that use were principally those due to the burning of discarded copies. Based on the assumption that 10 percent of the copies were discarded and burned, zinc emissions to the atmosphere during 1969 were approximately 1,500 tons.

Paints - Another large use of zinc oxide is in paints for exterior wood surfaces. In this application it has a number of desirable effects. It aids in mixing and grinding, improves drying and hardening of the paint film, reduces paint discoloration, improves mildew resistance and self-cleaning, and reduces chalking. Emulsion-type latex paint coatings for use on cement and masonry surfaces also require the use of zinc oxide for the same purpose as oil-base paints, with the additional benefit of helping to reduce can corrosion.

At the paint factory the zinc oxide is received in paper sacks and emptied into vats containing a liquid. There is a small amount of dusting as the sacks are emptied, and at most of the locations visited during this study there were ventilation systems. At some factories there were exhaust systems with hoods over the vats and a fan discharging to the atmosphere. At other plants the vats were entirely enclosed and the exhaust was through a bag filter. At one plant the men handling the sacks wore respiratory equipment. There were no hoods over the vats, but the entire building was ventilated. Usually there was some dust on the floor around the vats, and traces of zinc oxide remained in the empty bags which were either burned or discarded with the other trash.

There were no emission records available at any of the paint factories and there was no basis for an accurate estimate. Based on observations it is reasonable, however, to assume that the atmospheric emissions of zinc oxide do not exceed one pound per ton of zinc oxide processed. The quantity used in paint in 1969 was 25,170 tons, and emissions are estimated at 10 tons (Zn content).

Other - The miscellaneous uses of zinc oxide are numerous, collectively accounting for about 23 percent of the total consumption in 1969. In ceramics and glasses including glazes, enamels, and frits it is an essential ingredient. In glasses it reduces the melting time, lowers viscosity, and raises chemical and mechanical resistance. Up to 15 percent zinc oxide may be used for heat-resisting glass, technical glass, optical glass, selenium ruby glass, and yellow nickel glass. For special purposes the zinc oxide content is even higher, sometimes over 50 percent. In glazes it contributes to fusibility, increases resistance to thermal and mechanical shock, prevents crazing, improves luster, and enhances opacity.

Another application of zinc oxide is in porcelain enamels for sheet iron and vitreous enamels for cast iron. In these applications it contributes to electrical resistivity. These enamels are used extensively on refrigerators, ranges, washers, sinks, and toilet fixtures.

The principal sources of zinc emissions during the making of glass, glazes, and enamels are the initial dry mixing operations and the melting furnaces.

Miscellaneous uses of zinc oxide are relatively minor, none

accounting for more than 0.3 percent of the total use of zinc. Since emissions resulting from these uses cannot be calculated accurately, all factors have been considered and a conservative figure of 1,000 tons has been estimated by the Contractor as the zinc emissions to the atmosphere during 1969 due to the use of zinc oxide in ceramics, glass, feed additives, floor coverings, soaps, and other products.

Rolled Zinc

Rolled zinc is generally produced in all the usual forms of sheet, strip, plate, rod, and wire. For this purpose it is preferable to use high-grade zinc adding alloying metals such as copper, magnesium, manganese, chromium, and titanium in controlled amounts. A zinc content of 99.8 percent or more gives good drawing characteristics, and the alloy additions provide a material with a wide range of tempers and strengths. Rolled zinc may be buffed, painted, plated, lacquered, chemically colored, and enameled to provide a wide variety of finishes. Among its uses are photoengraving, lithography, dry cells, weather stripping, and many building applications.

The zinc and its alloying elements are usually melted in a reverberatory-type furnace, although induction furnaces may be used when careful product control is necessary. The furnace temperature for melting is about 850 to 950 F. After the melting operation, the zinc is cast into molds for rolling slabs. Prior to rolling operations, these slabs are then heated again to a temperature range of 300 to 500 F depending on the desired product. The rate of reduction during rolling is determined by the analysis of the metal, the type of

equipment, and the desired finish.

The manufacturing of photoengraving zinc follows approximately the same procedures as used in ordinary rolled zinc. In making these plates, virgin zinc (spelter) is purchased from a refinery and an electric induction furnace is used to remelt the spelter. The molds used are equipped to give controlled cooling for as perfect a slab as possible. Finally, molds are placed in a holding oven before rough rolling, cold rolling, and trimming. After the rolling the zinc plates are degreased, painted on the back with a special acid-, alkali-resistant material, and baked. Grinding, washing, polishing, inspection, and packing are the final steps. It might be noted that there is a large percentage of reject material throughout the operations due to the necessity for surface perfection on the plates, and this furnishes some portion of secondary zinc.

Rolled zinc sheets are used as press plates in offset lithography. These plates must have the tensile strength to allow clamping without distorting the plate cylinder, and toughness to resist fatigue and breakage. Zinc plates may have a plain or grained surface. The grained surface is presently most used. This is produced in a graining machine with steel

balls, an abrasive, and water. After graining, the plates are washed thoroughly and dried with a minimum of heat to prevent recrystallization of the zinc plate. The grained surface of a plate provides a tooth for the printing image and ink, and enables the plate to carry the proper amount of water in the non-printing areas. In many cases, after the completion of the press run, the zinc press plates are removed, cleaned, flattened, and regrained for future use.

Strip-rolled zinc is also used in manufacturing dry-cell batteries. It is soldered into a cylindrical shell, although currently the cans for standard flashlight-size batteries and smaller sizes are most often drawn zinc. Zinc chloride is also used in the paste which fills the battery can. Another dry battery, known as the flat-cell type, uses a flat piece of strip-rolled zinc to provide electrical contact between the combined cells within the battery.

A high-grade zinc with varying alloys provides a material with a wide range of temper and strength characteristics for building applications. Strip with lower alloy content is useful for flashings, valleys, corner bead, and other architectural uses. Higher alloys produce strip used as weather

strip, terrazzo strip, wall ties, moldings, and downspouts.

From the standpoint of air pollution, the production and use of rolled zinc does not appear to be a problem of any consequence. Manufacturers have advised that zinc emissions are negligible and air pollution control equipment is not required.

Zinc Sulfate

During 1969 about 30 percent of the zinc sulfate was used for agricultural purposes and 30 percent in the manufacture of viscose rayon fiber. The remainder was consumed in many minor process applications including clarification of glue, paint and varnish processing, electrogalvanizing solutions, froth flotation of minerals, and wood preservation.

Zinc sulfate is usually prepared by leaching roasted zinc ore concentrates with sulfuric acid solution and filtering out the residue. After removal of metal impurities, the solution may be evaporated and dryed in a kiln, a spray dryer, or other similar equipment.

Reports from 24 manufacturers that prepare or use zinc sulfate indicate that atmospheric emissions average not more than 0.5 pound of zinc per ton of zinc sulfate processed. During 1969 the zinc sulfate produced was 64,274 tons [1] (Zn content - 22,000 tons), and zinc emissions to the atmosphere totaled about 30 tons.

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[1] Minerals Yearbook, Bureau of Mines, 1969.

Miscellaneous

The miscellaneous uses of zinc which amounted to 94,000 tons during 1969 include the zinc dust and slab zinc consumed in the production of several light metal alloys, the desilverizing of lead, the manufacture of wet batteries, the production of bronze powder, and other minor uses not included in other sections of this report.

In the desilverizing of lead, the lead bullion gives up its silver content to zinc. In general the 2 processes used both include the "stirring-in" of zinc, cooling, skimming silver-zinc crusts, and distillation of crusts. During 1969 the slab zinc consumed for this purpose was 3,957 tons [1]. None of the smelting companies contacted during this study provided estimates of zinc emissions due to desilverizing operations.

Zinc is used as the anode of various "wet" batteries such as the Lalande cell, Eveready air cell, National Carbon air cell, and the comparatively new silver-zinc battery. The manufacturers of these batteries were contacted and without

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1 Minerals Yearbook: Bureau of Mines: 1969.

exception they reported that zinc emissions are negligible during manufacturing operations.

Zinc is a secondary or minor ingredient in many light metal alloys, including both the cast and wrought alloys of aluminum and magnesium. It is also frequently alloyed with tin as in aluminum solders, Britannia metal, pewter, and "Queen's metal". In silver solders the zinc content ranges from about 5 to 40 percent.

Estimates of zinc emissions to the atmosphere resulting from miscellaneous uses of zinc have been estimated by the Contractor almost entirely without assistance from industrial sources. Only 2 manufacturers provided emission estimates. More than 30 others stated their emissions were negligible; however, some defined negligible emissions as less than one percent loss of raw material. It is apparent there are some losses to the atmosphere during the desilverizing of lead and during alloying, as well as in the operations using smaller quantities of zinc.

During 1969 zinc emissions to the atmosphere due to processing and manufacturing operations are estimated by the Contractor at 100 tons, or approximately 1/10 of one percent of the zinc consumed for such miscellaneous purposes.

OTHER SOURCES OF ZINC EMISSIONS

COAL

A search has been conducted and information has been found regarding the zinc content of coal, ash of coal, and fly ash emissions from coal fired power plants.

With respect to fly ash, there is a study of emissions from coal fired power plants which shows the analysis of several fly ash samples. Six power boilers were tested, each a different type, and each value reported was the average of at least 2 tests. Two of the boilers were fired with Illinois coal; 2 burned Pennsylvania coal; one used some coal from Ohio and some from West Virginia; one burned part Kentucky and part West Virginia coal. The coal burned during the tests represented only a small portion of the coal mined in the various regions of the United States.

Zinc concentrations in the fly ash samples taken before fly ash collection ranged from 4.2 to 42 x 10^{-4} grains per scf [1].

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1. Cuffe, Stanley T. and Gerstle, Richard W.: "Emissions from Coal Fired Power Plants". Public Health Service Publication No. 999-AP-35; 1967.

The average was 18×10^{-4} grains per scf. Calculations have been made based on:

(a) 516,084,000 tons of bituminous and anthracite coal consumed in the United States during 1969 [1];

(b) 160 scf of flue gas per pound of coal;

(c) 18×10^{-4} grains per scf zinc concentration;

(d) 85 percent efficiency of control; and

(e) 90 percent application of control.

The zinc emissions calculated in this manner totaled 5,000 tons.

$$\frac{516,084,000 \times 160 \times 18 \times 10^{-4} \times 2,000}{7,000 \times 2,000} \left[1 - (0.85 \times 0.90)\right] = 5,000$$

During the combustion of coal, zinc is discharged with the ash; part with the bottom ash and part with the fly ash. The fly ash averages about 65 percent of the total ash.

Many samples of coal have been analyzed and the zinc content reported as shown in Table VIII. Calculations have been made based on:

(a) 516,084,000 tons of bituminous and anthracite coal consumed in the United States during 1969 [1].

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1 - Minerals Yearbook: Bureau of Mines 1969.

(b) 54.6 ppm average zinc concentration in coal;

(c) fly ash 65 percent of total ash;

(d) 85 percent efficiency of control; and

(e) 90 percent application of control.

The zinc emissions calculated in this manner totaled 4,310 tons.

$$516,084,000 \times 54.6 \times 10^{-6} \times 0.65 \left[1 - (0.85 \times 0.90)\right] = 4,310$$

In this report the figure of 4,310 tons is used as the zinc emissions to the atmosphere during 1969 due to the combustion of coal.

TABLE VIII

AVERAGE MINOR ELEMENT CONTENTS OF COAL FROM VARIOUS REGIONS OF THE UNITED STATES - PPM

Region	Ash Content of Coal - %	Zn Content of Coal - ppm
Northern Great Plains	13.42	59.0
Eastern Interior	6.16	44.0
Appalachian	6.11	7.6
Western and Southwestern	NR*	108.0
Average Zinc Content in Coal		54.6

*Not reported

NOTE - The above table based on Geological Survey Bulletins 1117-C and 1117-D, 1966 and 1967.

OIL

In order to estimate the zinc emissions to the atmosphere due to the combustion of fuel oil, it was necessary to determine the zinc content and the quantity of oil received from numerous foreign and domestic sources. Some data was obtained from publications, and some from major oil companies.

The zinc content in crude was shown in more than 100 samples of domestic oil; however, the situation was different with respect to the metal content of residual oils. The only reliable information available from published sources was that regarding nickel and vanadium. The unpublished data available consisted of the analyses of 3 samples of imported residual oil which was analyzed for the Environmental Protection Agency, Office of Air Programs, during 1971. The average zinc content of the 3 samples was 4.17 ppm.

The residual oil used in the United States during 1969, exclusive of use in vessels, was 639 million barrels. This oil containing zinc at 4.17 ppm (average) was used by industrials, electric utility companies, railroads, oil companies, and the military, as well as for heating (Table IX).

TABLE IX

RESIDUAL FUEL OIL DATA

Residual Fuel Oil Burned - 1969 (bbls)	639,048,000
Pounds per Barrel	340
Zinc Content of Oil (ppm)	4.17

Based on the data in Table IX, the zinc emissions to the atmosphere due to the combustion of residual oil totaled 450 tons during 1969.

Due to the scarcity of data on zinc and other trace metals in oil, the emissions may be considerably more than estimated. The burning of fuel oil could be a major localized source of zinc emissions.

IRON AND STEEL

Steel mills are important sources of zinc emissions to the atmosphere. Zinc in the iron ore is discharged to the atmosphere from the blast furnace as the ore is reduced to pig iron and zinc in the scrap is discharged from open-hearth, basic oxygen, and electric furnaces as pig iron and scrap are converted to steel.

Blast Furnaces - As the gas leaves the blast furnace, it contains large quantities of particulates averaging about 150 pounds per ton of pig iron [1]; however, it is subsequently cleaned and used as fuel. The gas cleaning is accomplished in 2 or 3 stages, and the annual overall efficiency is an estimated 97 percent.

During 1969, the pig iron produced in the United States totaled 95,472,000 tons [2]. The estimated zinc content of the particulate from blast furnaces was 0.5 percent [3]. Zinc emissions to the atmosphere from blast furnaces totaled 1,070 tons.

1- "Air Pollutant Emission Factors"; Environmental Protection Agency; Preliminary Document; Apr., 1971.

2- Minerals Yearbook; Bureau of Mines; 1969.

3- Varga, J. Jr., et al; "A Systems Analysis Study of the Integrated Iron and Steel Industry"; Battelle Memorial Institute; Columbus, Ohio; May, 1969.

Open-Hearth Furnaces - The overall operating cycle of the open-hearth furnace is about 10 hours. Even though fumes are discharged continuously at varying rates, average emission factors have been established for operation both with and without oxygen lancing. With oxygen lancing, the factor for uncontrolled emissions is 21 pounds of particulate per ton of steel. Without lancing, the factor is 8 pounds per ton. The degree of emission control is estimated at 40 percent, and the average emission factor (controlled) for all open-hearth furnace operations is 10.2 pounds of particulate per ton of steel produced [1].

The mean particle size of the dust is generally considered to be 0.5 micron [2] and the average zinc content 12.5 percent [3]. During 1969 the steel produced in open-hearth furnaces was 60,894,000 tons [4], and the zinc emissions to the atmosphere totaled 39,000 tons.

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1. "Emissions, Effluents and Control Practices", Environmental Protection Agency: Study in Progress (unpublished) 1970.

2. Aberlow, E. B. "Modification to the Fontana Open-Hearth Precipitators", JAPCA 7 May, 1957.

3. "Air Pollution Engineering Manual", Public Health Service Publication No. 999-AP-40 p. 243 1968.

4. Minerals Yearbook, Bureau of Mines 1969.

Basic Oxygen Furnaces - The operating cycle of the basic oxygen furnace is normally about one hour, and large quantities of gas and particulate are discharged to the atmosphere throughout the operation. The emission factor for this type of furnace has been estimated at 46 pounds of particulate per ton of steel [1], and the degree of emission control at 97 percent.

During 1969 the steel produced in basic oxygen furnaces was 60,236,000 tons [2], and the estimated zinc content of the particulate emissions 2.24 percent [3]. Zinc emissions to the atmosphere from basic oxygen furnaces totaled 900 tons.

1- "Air Pollutant Emission Factors". Environmental Protection Agency: Preliminary Document. Apr., 1971.

2- Minerals Yearbook. Bureau of Mines: 1969.

3- Varga, J. Jr., et al: "A Systems Analysis Study of the Integrated Iron and Steel Industry". Battelle Memorial Institute, Columbus, Ohio. May, 1969.

Electric Furnaces - Electric arc furnaces are used extensively for the production of alloy steels and the raw material used is principally scrap iron. Emissions generated during operation consist of fume and dust emitted throughout the charging and refining operations. While charging, the top is open to receive the cold metal, and the exposure of the cold charge to the high temperature inside the furnace results in the generation of large quantities of fume.

Particulate emissions from electric arc furnaces have been estimated with and without oxygen lancing at 11 pounds and 7 pounds per ton of steel, respectively [1]. The degree of control is estimated at 78 percent, and the average emission factor (controlled) at 2.5 pounds of particulate per ton of steel produced.

During 1969 the steel produced in electric arc furnaces was 20,132,000 tons [2]. The zinc content of the particulate is estimated at 29.6 percent [3], and zinc emissions to the atmosphere from electric furnaces totaled 7,400 tons.

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1. "Air Pollutant Emission Factors", Environmental Protection Agency; Preliminary Document, Apr., 1971.

2. Minerals Yearbook, Bureau of Mines, 1969.

3. Coulter, R. S. "Smoke, Dust, Fumes Closely Controlled in Electric Furnaces" Iron Age 173 Jan 14, 1954.

FOUNDRIES

During this study spectrographic analyses of dust samples from 3 iron foundries have been examined and they show zinc is present in all samples, the content ranging from 0.2 to 2.0 percent [1].

The cupola is the most popular method for producing cast iron. The rate of particulate emissions from gray iron cupolas has been reported as 4 to 26 pounds per ton of process weight not including emissions from materials handling, charging, or other non-melting operations.

Based on information obtained from industry, the particulate emission factor is estimated at 22 pounds per ton of process weight, including melting and non-melting operations. The degree of emission control is approximately 25 percent. Calculations show that with 1.1 percent zinc in the particulate, the emission factor is 0.18 pound of zinc per ton of process weight.

During 1969 the pig iron and scrap used by iron foundries

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1 Private communication.

totaled 18,594,000 tons [1]; therefore, zinc emissions to the atmosphere due to the production of cast iron were 1,700 tons.

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1 Minerals Yearbook. Bureau of Mines. 1969.

INCINERATION

A recent report concerning the burning of sewage and sludge indicates the present burning rate in the United States is about 2,000 tons per day [1]. Based on an average zinc content of 2,411 ppm [2], the atmospheric emissions of zinc due to the burning of sewage and sludge during 1969 were 1,750 tons.

The burning of refuse and garbage is also a source of zinc emissions to the atmosphere. It has been estimated and reported that approximately 50 percent of all the generated waste in the United States, or about 5 pounds per person per day, is burned by various combustion methods [3]. Emission data have also been reported which indicate that incinerator emissions range from 3 to 28 pounds per ton of refuse burned, while the zinc content of the ashed material is from

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1. Private communication with the Federal Water Pollution Control Authority.

2. Clark, L. J. and Hill, W. L. "Occurrence of Manganese, Copper, Zinc, Molybdenum, and Cobalt in Phosphate Fertilizers and Sewage Sludge" Journal of the A.O.A.C. 41 No. 3 1958.

3. "Air Pollutant Emission Factors" Environmental Protection Agency Preliminary Document Apr., 1971.

one to 10 percent [1]. Based on an average of 15 pounds of particulate per ton of refuse burned and a zinc content of 2 percent, the zinc emissions to the atmosphere are about 26,200 tons per year.

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1. "Air Quality Criteria for Particulate Matter" National Air Pollution Control Administration Publication No. AP-49 Jan., 1969.

UPDATING OF EMISSION ESTIMATES

The emissions and emission factors presented in this report are the result of calculations based principally on information obtained from industrial sources. They are specifically for the year 1969, but may be updated at any time when additional information is available. Either of the 2 methods described herein may be used for updating; however, the longer procedure, referred to as Method A, will yield results that are much more reliable.

The procedures to be followed with Method A are essentially the same as those used during the original study, which are described briefly as follows. More than 175 inquiries were sent to processing and reprocessing companies by mail, or delivered during personal visits to plant sites. There was no reply from 58 companies even after 2 or 3 follow-up letters. Another 36 companies answered but did not provide data. Some refused, but most of them claimed they did not have the information readily available. There were 82 companies that furnished all or part of the data requested, and this was the basis for emissions and emission factors set forth in this report.

All of the companies that produce primary slab zinc were requested to provide the essential data required for the study. Information was obtained concerning 2 of the 5 electrolytic plants, 3 of the 5 horizontal-retort plants, and 3 of the 4 vertical-retort plants. Based on the data obtained, emission factors were calculated and reported for each type plant.

With respect to secondary zinc, about 50 percent of the companies were contacted and the data obtained concerned nearly 30 percent of the production capacity. The reprocessing companies that provided information represented about 20 percent of the industry capacity.

Regardless of the method selected, the first step to be taken when updating the emission estimates is to obtain the latest issue of the Bureau of Mines Minerals Yearbook, Volume I-II, which is normally available within 16 or 18 months after the end of the calendar year (preprints of individual sections are usually available sooner). This publication shows the quantity of ore mined and the zinc produced in the United States, as well as the quantities imported and exported. It also shows the amount of slab zinc consumed and the various purposes for which it was used. In this one publication, all of the

information is available that is required to update the material flow chart for zinc.

When using Method A, the emission factors must be revised by contacting industry to determine the improvements in air pollution collection equipment efficiency, and other processing changes affecting zinc emissions. The revised emission factors may then be used with the production quantities obtained from the Minerals Yearbook or other referenced sources.

Method B is considerably shorter than Method A and less reliable. The only requirement is to revise the material flow chart according to the most recent published data and apply the emission factors shown in this report. In reality, this method is only a partial updating. There is no determination regarding improvements in air pollution control, a shift in production to more efficient plants, or any other considerations affecting emission factors. The advantage is that the report can be updated within a few days rather than several months.

To update zinc emissions from metallurgical processing, secondary production, zinc-base alloy processing, zinc oxide production, and the iron and steel industry, it is

preferable to use Method A. The remaining emissions shown in this report may be updated by Method B without introducing an appreciable error into the results.

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